RAW MATERIALS

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CLAY SHALE FROM THE DZHERDANAKSKOE DEPOSIT: A HIGH-QUALITY CERAMIC MATERIAL

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The properties of clay shale from the Dzherdanakskoe deposit (Uzbekistan) are investigated. It is established that a mullite-resembling phase with an elevated silicon oxide content is formed in thermal treatment. The possibility of producing refractories, porcelain, and faience based on material from this deposit is demonstrated.

The Dzherdanaskskoe deposit of clay shale is located in the foothill part of the eastern slope of the Kuchitangtau mountain ridge (Uzbekistan). The refractory materials from this deposit, namely, crystalline quartzite and clay shale, have been known since 1942. They were first described by E. I. Sarychev. The rather rare properties of the clay shale from this deposit were noted by D. N. Poluboyarinov [1]. However, until recently, the materials from this deposit have not been used. The present study is carried out to fill this gap.

Clay shale has the appearance of a dense rock with a color ranging from dark gray to black. The refractoriness of the shale varies from 1610 to 1770°C. The productive strata of this rock are comprised by non-uniform alternating layers and blocks of quartzite and clay shale.

Clay shale is arbitrarily divided into three groups: I) kaolinite; the bulk of the rock consists of kaolinite, with mica and quartz detritus present as impurities; II) mica; the bulk of the rock consists exclusively of a mica-resembling material, and impurities are quartz detritus; III) mixed type; kaolinite and the mica-resembling mineral are present in approximately equal quantities, and quart detritus are encountered as inclusions.

The chemical composition of the material is as follows: (here and elsewhere, wt.%): 49.43 – 57.76 SiO_2, 28.34 – 32.03 Al_2O_3, 0.15 – 0.35 TiO_2, 0.35 – 1.10 Fe_2O_3, 0.25 – 1.30 CaO, traces — 0.01 MgO, traces — 0.85 Na_2O, 2.93 – 7.94 K_2O, 6.84 – 10.32 calcination loss. The clay shale from the Dzherdanakskoe deposit has a high potassium modulus and a low content of colorant iron and titanium oxides.

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Electron-microscope photos of the clay shale are shown in Fig. 1. Differential thermal analysis of the rock yielded a pattern typical of kaolinite with a superimposition of the thermal effects of mica; however, the first exothermic effect of kaolinite is shifted toward low-temperature range (910°C). Comparison of the data of the microanalysis and the x-ray analysis (Fig. 2) made it possible to identify the main components of the rock, i.e., kaolinite and hydromica of the muscovite type.

Fig. 1. Electron microscope photos of natural clay shale (*a*) and clay shale heat-treated at 1350°C (*b*).

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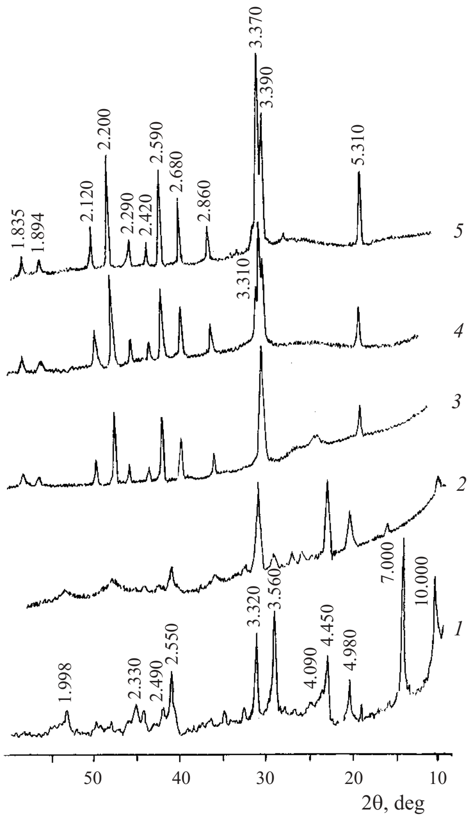

Fig. 2. Diffraction patterns of natural clay shale (*1*) and clay shale heat treated at 950 (*2*), 1350 (*3*), 1400 (*4*), and 1700°C (*5*).

Rock samples heat-treated in a temperature range of 500 – 1700°C with a 1-h exposure at the maximum temperature were subjected to an x-ray phase analysis. The diffraction patterns registered the destruction of kaolinite and hydromica and the formation of mullite under the temperatures of 950 – 1100°C (depending on the kaolinite-to-hydromica ratio in the initial rock). The reflections of quartz were identified as well, which transforms into a melt at 1700°C.

The results of electron-probe microanalysis (JEOL, Japan) of the crystalline and amorphous components of the material heat-treated at 1350°C are given in Table 1.

The molar ratio of $Al_2O_3 : SiO_2$ in the vitreous phase varies from 0.4 to 0.5, whereas the fluctuation in the crystalline phase is minimal and this ratio is equal to 0.6. It is worth noting that a greater part of the titanium oxide is concentrated in mullite (which is the crystalline component) and potassium

TABLE 1

Phase	Weight content, %				
	Al_2O_3	SiO_2	K_2O	TiO_2	Fe_2O_3
Vitreous	39.97	55.59	4.73	–	0.36
	47.34	50.02	2.71	0.06	0.46
Crystalline	48.16	48.01	3.44	0.58	0.33
	49.45	48.30	2.51	0.10	0.39

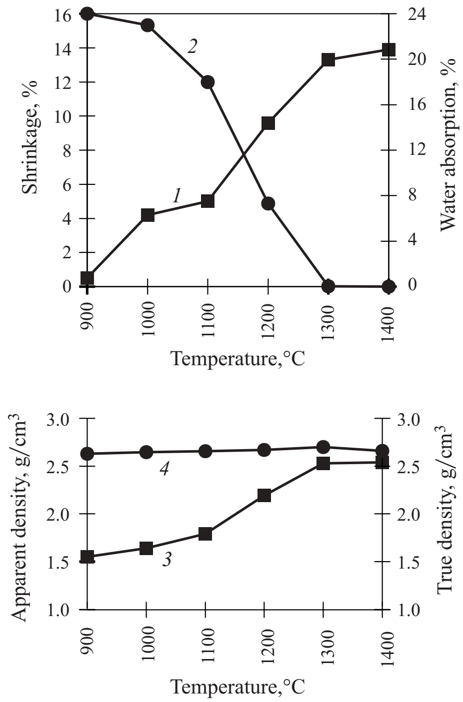

Fig. 3. Variations in shrinkage (*1*), water absorption (*2*), apparent density (*3*), and true density (*4*) depending on the firing temperature.

and iron oxides are comparatively evenly distributed among the vitreous and the amorphous phases.

The existence of a stable compound of aluminum and silicon oxides with a composition of $Al_2O_3 \cdot SiO_2$ and a mullite-resembling structure was noted earlier [2]. The specified compound has good technical properties; however, it is formed only in a reducing medium, and protracted heating in an oxidizing medium transforms it into stoichiometric mullite $3Al_2O_3 \cdot 2SiO_2$ and cristobalite [3].

The emergence of the mullite-like phase with en elevated silica content in heat treatment of the clay shale from the Dzerdanakskoe deposit can be accounted for by the presence of organic compounds in this rock, which create a local reducing medium in firing, the finely dispersion nature of the components, and the sufficiently high content of potassium oxide.

As a result of a thermal treatment of the clay shale, mullite with prismatic crystals is synthesized (Fig. 1*b*) and a vitreous phase is formed. The quantity of the vitreous phase increases with increasing content of the mica-resembling mineral in the material. The maximum whiteness of sintered samples is 90%. The mechanical activation of clay shale in fine milling results in the material acquiring plastic properties.

The sintering kinetics of the clay shale was investigated on the respective samples. The results obtained on samples molded from the plastic mixture based on group III of the material are shown in Fig. 3.

The maximum bending strength of the sintered samples was 70 MPa, and the TCLE in the temperature interval of

$20 – 600°C$ was $4.8 \times 10^{-6}\ K^{-1}$. The clay shale was tested under laboratory conditions to produce refractories (group I) and fine ceramics (groups II and III).

The preliminary study established the possibility of using clay shale as the main component and as a binder in the production of refractories. Experimental samples of faience and porcelain were obtained that had good whiteness.

Thus, clay shale from the Dzherdanakskoe deposit is a high-quality mineral material suitable for production of a wide variety of engineering and household products.

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